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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the optical solid molding method using the resin composition for optical solid modeling and this which are high sensitivity to irradiation energy about the optical solid molding method which used the resin composition for optical solid modeling, and this in detail.

[0002]

[Description of the Prior Art]As indicated as optical solid modeling to JP,60-247515,A, By putting the various resin which has a photoresist into a container, and glaring continuously from the upper part by irradiating the arbitrary parts of this resin with beams, such as argon laser, a helium cadmium laser, and a semiconductor laser, The above-mentioned beam irradiation part of resin is stiffened, this creates the target flat surface, and a hardening layer is formed. Then, it is the method of obtaining the three-dimensional solid thing made into the purpose, by supplying the resin which has the above-mentioned photoresist by one more layer on this hardening layer, hardening this like the above, performing lamination operation of obtaining the hardening layer which followed the above-mentioned hardening layer, and repeating this operation.

[0003]Conventionally, as resin used for the above-mentioned optical solid modeling, there is a radical polymerization nature resin composition first, for example, the resin composition for solid modeling centering on an acrylic resin (meta) is indicated by JP,2-228312,A and JP,5-279436,A. Liquefied resin and the resin for optical solid modeling in which specific gravity difference contains seemingly the fine grain which is less than 0.2 are indicated by JP,2-145616,A for the purpose of reduction of modification. To JP,3-15520,A, for the precision improvement of shaping material, an ethylene system unsaturated monomer, The report of the constituent in which the report of the constituent which consists of a photoinitiator and an

insoluble potential radiation polarization substance becomes JP,3-41126,A from an ethylene system unsaturated monomer, a photoinitiator, and a soluble potential radiation polarization substance again is made, respectively. The resin composition which contains in JP,4-85314,A further again the compound and polymerization initiator which have silicone urethane acrylate and a polyfunctional ethylenic unsaturated bond is indicated.

[0004]The cationic polymerization nature resin composition is known as other resin for optical solid modeling. For example, to JP,1-213304,A, the invention containing an energy-line hardening type cationic polymerization nature organic compound and an energy-line susceptibility cationic initiator is indicated. Resin of the low shrinkage which blended the energy-line hardening type radical polymerization nature organic compound with the energy-line hardening type cationic polymerization nature organic compound in part, and high resolution is indicated by JP,2-28261,A. The resin composition which blended vinyl ether resin, an energy-line susceptibility cationic initiator, radical hardening resin, and an energy-line susceptibility radical polymerization initiator with the epoxy resin is indicated by JP,2-80423,A. Further again to JP,2-75618,A. An energy-line hardenability cationic polymerization nature organic compound, an energy-line susceptibility cationic initiator, The resin composition for optical modeling containing an energy-line hardenability radical polymerization nature organic compound, an energy-line susceptibility radical polymerization initiator, and hydroxyl group content polyester is indicated.

[0005]The oxetane monomer which has one or the plurality of an oxetane ring which is 4 membered-ring cyclic ether as a polymerization nature functional group in recent years, equivalent to a corresponding epoxy monomer or having a photoresist beyond it is reported (journal OBU macromolecular science A -- 29 volumes) No. 10, 915 pages, 1992, said A30 volume, No. 2&3, 173 pages, 1993, said A30 volume, No. 2&3, 189 pages, 1993. The photo-curing setup-of-tooling product which uses a polyfunctional oxetane monomer as the main ingredients is proposed by JP,6-16804,A as what has quick hardenability. The compound which has two or more oxetane rings in a molecule at JP,7-53711,A, The activity energy-line hardening setup-of-tooling product which consists of a compound which makes cationic polymerization start by the exposure of the compound which has one or more oxirane rings in a molecule, and an activity energy line, The activity energy-line hardening setup-of-tooling product which consists of a compound which makes JP,7-62082,A start cationic polymerization by the exposure of the compound which has one oxetane ring in a molecule, the compound which has one or more oxirane rings in a molecule, and an activity energy line is indicated, respectively.

[0006]

[Problem(s) to be Solved by the Invention]However, the resin composition for optical solid modeling which made radical polymerization nature resin and it the main ingredients, Since the

radical polymerization is used, even when which resin (constituent) is used, the hardening inhibition by oxygen takes place, Since the curing rate at the time of hardening became low, "postcure processing" which gives the light or the heat which certainly participates in hardening at the time of modeling needed to be carried out, and it had a fault which is easy to transform shaping material on the occasion of curing treatment after this. The contraction at the time of hardening of these resin was also large, and it was difficult to obtain the shaping material of a desired size.

[0007]JP,1-213304,A, JP,2-28261,A, and resin for cation hardening type optical solid modeling like a JP,2-75618,A statement, Have the outstanding feature that postcure processing is unnecessary and little modification is, and since the hardening inhibition by oxygen does not take place but hardening advances even after optical interception with the live children in resin, the contraction at the time of hardening is also small, and easy to obtain the shaping material of a desired size, but. There was a fault that sensitivity was not enough, to irradiation energy.

[0008]About the activity energy-line hardenability constituent which uses the compound which has the above-mentioned oxetane ring, it is still unknown about the cure shrinkage. Namely, in order to laminate many hardening layers in optical solid modeling, in size, the influence of the cure shrinkage of the resin given to the dimensional accuracy of shaping material as compared with the use of other photo-setting resins comes, and fries resin for optical solid modeling eight, It was unknown whether the compound which has these oxetane rings could use it for optical solid modeling.

[0009]Then, the hardening inhibition by oxygen does not take place, but the purpose of this invention has unnecessary postcure processing, It has the outstanding feature that little modification is, and it is small, the contraction at the time of hardening is also easy to obtain the shaping material of a desired size, and it is in moreover providing the optical solid molding method using the resin composition for optical modeling and this with high sensitivity to irradiation energy.

[0010]

[Means for Solving the Problem]In order to solve an aforementioned problem, a resin composition for optical solid modeling of this invention contains a cationic polymerization nature organic substance which has an oxetane ring in (1) molecule, and (2) energy-line susceptibility cationic initiator as an indispensable constituent. It is a resin composition for optical solid modeling.

[0011]This invention is a resin composition for optical solid modeling containing further cationic polymerization nature organic substances other than a compound which has an oxetane ring in (3) molecules in the above-mentioned resin composition for optical solid modeling.

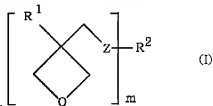
[0012]This invention is a resin composition for optical solid modeling containing (4) radical-polymerization nature organic compound and (5) energy-line susceptibility radical

polymerization initiator further in the above-mentioned resin composition for optical solid modeling.

[0013]Further again this invention on the arbitrary surfaces of an energy-line hardenability resin composition. Irradiate with an energy line, stiffen the energy ray surface of this resin composition, form a hardening layer of desired thickness, and the above-mentioned resin composition for optical solid modeling is further supplied on this hardening layer, In an optical solid molding method which obtains a three-dimensional solid thing by performing lamination operation of obtaining a hardened material which stiffened this similarly and followed the above-mentioned hardening layer, and repeating this operation, The above-mentioned energy-line hardenability resin composition is an optical solid molding method being the above-mentioned resin composition for optical solid modeling.

[0014]

[Embodiment of the Invention]As a cationic polymerization nature organic substance which has an oxetane ring, various things can be used into (1) molecule of this invention, and it is



following general formula (I) as a desirable compound,

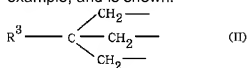
It can come out and the compound expressed can be mentioned.

[0015]Here, in formula (I), m is 1, 2, 3, or 4. When m is 1, Z is an oxygen atom or a sulfur atom, and R¹ A hydrogen atom, The alkyl group of 1-6 carbon numbers, such as a fluorine atom, a methyl group, an ethyl group, a propyl group, or a butyl group, They are the fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, a furil group, or a thienyl group, R² The alkyl group of 1-6 carbon numbers, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, or a butyl group, 1-propenyl group, 2-propenyl group, a 2-methyl-1-propenyl group, The alkenyl group of 1-6 carbon numbers, such as a 2-methyl-2-propenyl group, 1-butenyl group, 2-butenyl group, or 3-butenyl group, Aryl groups, such as a phenyl group, benzyl, fluorobenzyl, a methoxybenzyl group, or a phenoxyethyl group, The alkyl carbonyl group of 1-6 carbon numbers, such as a propylcarbonyl group, a butyl carbonyl group, or a pentyl carbonyl group, The alkoxy carbamoyl group of 1-6 carbon numbers of the alkoxy carbonyl group of 1-6 carbon numbers, such as an ethoxycarbonyl group, a propylcarbonyl group, or a butyl carbonyl group, an ethoxycarbamoyl group, a propylcarbamoyl group, or a butylcarbamoyl group, etc. are mentioned.

[0016]When m is 1, R¹ has a preferred thing of a low-grade alkyl group, and its thing of an ethyl group is still more preferred. R² is a hydrogen atom, a butyl group, and benzyl preferably.

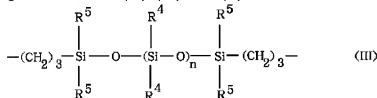
Z is an oxygen atom preferably.

[0017]When m is 2, 3, or 4, Z is an oxygen atom or a sulfur atom. R^1 is the alkyl group of 1-6 carbon numbers, such as a hydrogen atom, a fluorine atom, a methyl group, an ethyl group, a propyl group, and a butyl group, a fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, or a furil group. R^2 is the line of the carbon numbers 1-12 or the branching alkylene group, line, or branching poly (oxyalkylene) group which is following general formula (II), for example, and is shown.

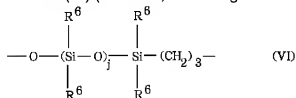


[0018]In the above-mentioned formula (II), R^3 is low-grade alkyl groups, such as a methyl group, an ethyl group, or a propyl group.

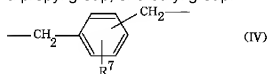
[0019] R^2 may also be a multivalent basis chosen from the group which consists of following general formula (III), (IV), and (V).



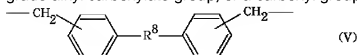
[0020]In formula (III), n is an integer of 0-2000. R^4 may be the same, or may differ and A methyl group, an ethyl group, It is a basis chosen from the group which comprises the alkyl group of 1-10 carbon numbers, such as a propyl group or a butyl group, and following general formula (VI) (however, it is that general formula (VI) is chosen as R^4 at the time of m= 3 or 4.).



[0021]In formula (VI), j is an integer of 0, or 1-100, and R^6 is alkyl which has a carbon atom of 1-10. R^5 is an alkyl group of the carbon numbers 1-10, such as a methyl group, an ethyl group, a propyl group, or a butyl group.

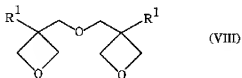
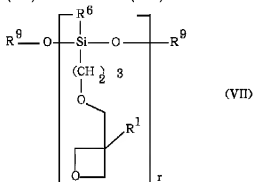


[0022] R^7 in formula (IV) A hydrogen atom, a methyl group, an ethyl group, They are the alkyl group of 1-10 carbon numbers, such as a propyl group or a butyl group, the alkoxy group of 1-10 carbon numbers, a halogen atom, a nitro group, a cyano group, a sulfhydryl group, a low-grade alkyl carboxylate group, or a carboxyl group.



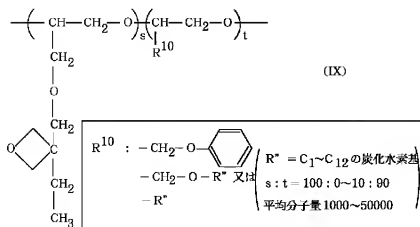
[0023] In formula (V), R^8 is an oxygen atom, a sulfur atom, NH, SO, SO_2 , CH_2 , $C(CH_3)_2$, or $C(CF_3)_2$. When m is 2, 3, or 4, the thing of a low-grade alkyl group has [in / at this invention / the above-mentioned formula (I)] preferred R^1 , and the thing of an ethyl group is more preferred. As R^2 , the thing of an ethyl group has preferred R^3 in the basis whose R^7 is a hydrogen atom, a hexamethylene group, and formula (II) in formula (IV). R^5 and R^6 are methyl groups preferably. Z is an oxygen atom preferably.

[0024] As desirable examples other than the above, the compound of following general formula (VII) and formula (VIII) can be mentioned.

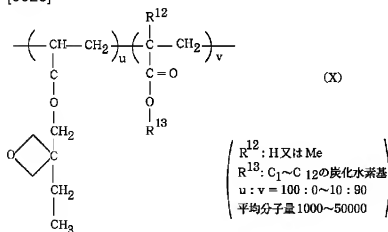


In formula (VII), r is an integer of 25-200 and R^9 is the alkyl group or trialkylsilyl group of the carbon numbers 1-4.

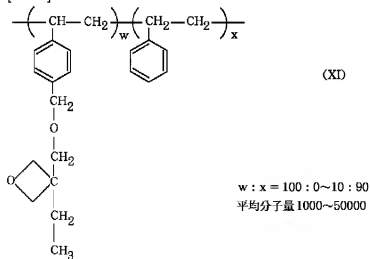
[0025] The oxetane compound of the structure shown in (XI) from following general formula (IX) can also be used.



[0026]



[0027]



[0028]The compound which has two or more oxetane rings in one molecule in this invention is still more preferred.

[0029]In this invention, more than two sorts or it of the compound which has an oxetane ring in

the above-mentioned molecule can be used together.

[0030]With (2) energy-line susceptibility cationic initiator used for this invention. It is a compound with possible making the substance which makes cationic polymerization start more by energy-line exposure emit, and especially a desirable thing is the double salt which is onium salt which emits Lewis acid by exposure, or its derivative. As a typical thing of this compound, the salt of the positive ion and negative ion which are expressed with general formula and $[A]^{m+}[B]^{m-}$ can be mentioned.

[0031]As for positive ion $[A]^{m+}$, it is preferred here that it is onium, and the structure can be expressed with $[(R^{14})_aQ]^{m+}$, for example.

[0032]Here, carbon numbers are 1-60 and R^{14} is an organic basis which may also contain atoms other than a carbon atom how many. a -- 1-5 -- it is an integer. a R^{14} is independence respectively, may be the same or may differ. As for at least one, it is preferred that it is an organic basis like the above which has an aromatic ring. Q is the atom or atom group chosen from the group which consists of S, N, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, F, and N=N. When the valence of Q in positive ion $[A]^{m+}$ is set to q, it is required to realize the relation which becomes in $m=a-q$ (however, N=N is treated as the valence 0).

[0033]As for negative ion $[B]^{m-}$, it is preferred that it is a halogenide complex, and the structure can be expressed for example, with $[LX_b]^{m-}$.

[0034]Here, L is the metal or semimetal (Metalloid) which is a neutral atom of a halogenide complex, and is B, P, As, Sb, Fe, Sn, Bi, aluminum, Ca, In, Ti, Zn, Sc, V, Cr, Mn, Co, etc. X is a halogen atom. b -- 3-7 -- it is an integer. When the valence of L in negative ion $[B]^{m-}$ is set to p, it is required to realize the relation which becomes in $m=b-p$.

[0035]As an example of negative ion $[LX_b]^{m-}$ of the above-mentioned general formula, tetrafluoroborate $(BF_4)^-$, Hexafluorophosphate $(PF_6)^-$, hexafluoroantimonate $(SbF_6)^-$, hexafluoroarsenate $(AsF_6)^-$, hexachloro antimonate $(SbCl_6)^-$, etc. are mentioned.

[0036]The thing of the structure expressed with $[LX_{b-1}(OH)]^{m-}$ can also be preferably used for negative ion B^{m-} . L, X, and b are the same as that of the above. in addition, as negative ion which can be used, Perchlorate ion $(ClO_4)^-$, trifluoromethyl sulfite ion $(CF_3SO_3)^-$, fluorosulfonic acid ion $(FSO_3)^-$, toluenesulfonic acid negative ion, trinitrobenzenesulfonic acid negative ion, etc. are mentioned.

[0037]It is effective especially to use following I - Ha's aromatic onium salt also in such onium

salt in this invention. Out of these, it is independent about one of them, or two or more sorts can be mixed and used.

[0038]b) Aryldiazonium salt, such as phenyldiazonium hexafluorophosphate, 4-methoxyphenyldiazonium hexafluoroantimonate, and 4-methylphenyldiazonium hexafluorophosphate [0039]**) Diaryliodonium salt, such as diphenyliodoniumhexafluoroantimonate, JI (4-methylphenyl) iodonium hexafluorophosphate, and JI (4-tert-butylphenyl) iodonium hexafluorophosphate [0040]**) Triphenylsulfonium hexafluoroantimonate, tris (4-methoxyphenyl) sulfonium hexafluorophosphate, Diphenyl-4-thio phenoxyphenyl sulfoniumhexafluoroantimonate, Diphenyl-4-thio phenoxyphenyl sulfonium hexafluorophosphate, 4,4'-bis(diphenylsulfonio) phenylsulfide bis-hexafluoroantimonate, 4,4'-bis(diphenylsulfonio)phenylsulfide bis-hexafluorophosphate, 4,4'-screw [JI (beta-hydroxyethoxy) phenylsulfonio] phenylsulfide bis-hexafluoroantimonate, 4,4'-screw [JI (beta-hydroxyethoxy) phenylsulfonio] phenylsulfide bis-hexafluorophosphate, 4-[4'-(benzoyl) phenylthio] phenyl-di-(4-fluorophenyl) sulfoniumhexafluoroantimonate, Triarylsulfonium salts, such as 4-[4'-(benzoyl) phenylthio] phenyl-di-(4-fluorophenyl) sulfonium hexafluorophosphate, etc. are preferred.

[0041]moreover -- in addition -- as a desirable thing (eta⁵-2,4-cyclopentadiene 1-yl) [(1,2,3,4,5,6, -eta) - (1-methylethyl) benzene] - Iron-arene complexes, such as iron hexafluorophosphate, The mixture of aluminium complexes, such as tris(acetylacetonate) aluminum, tris(ethyl acetonate ASETATO) aluminum, and tris(salicyl ARUDEHIDATO) aluminum, and silanols, such as a triphenylsilanol, etc. are mentioned. It is preferred to use aromatic iodonium salt, aromatic sulfonium salt, and an iron-arene complex from a viewpoint of a practical use side and photosensitivity also in these.

[0042]With cationic polymerization nature organic substances other than the compound which has an oxetane ring in (3) molecules used for this invention. With the compound which causes polymers-izing or crosslinking reaction by the energy-line susceptibility cationic initiator activated by energy-line exposure, substances other than the compound which has an oxetane ring in a molecule are said.

[0043]For example, it is a cyclic ether compound [other than an epoxy compound and the compound which has an oxetane ring], annular lactone compound, cyclic acetal compound, annular thioether compound, and spiroortho ester compound, a vinyl compound, etc., and these one sort or two sorts or more can be used. Receiving especially is easy and the epoxy compound convenient handling is suitable. As this epoxy compound, an aromatic epoxy compound, an alicycle fellows epoxy compound, an aliphatic series epoxy compound, etc. are suitable.

[0044]The polyhydric phenol which has at least one aromatic ring as an example of said aromatic epoxy resin. Or glycidyl ether, epoxy novolak resin, etc. of a compound to which alkylene oxide was made to add further are raised to poly glycidyl ether of the alkylene oxide

adduct, for example, bisphenol A, the bisphenol F, or these.

[0045]As an example of said alicycle fellows epoxy resin, Cyclohexane oxide and the cyclopentene oxide content compound which are obtained by epoxidating with an oxidizer poly glycidyl ether or the cyclohexene of polyhydric alcohol which has at least one alicyclic ring, and a cyclopentene ring content compound are mentioned. For example, hydrogenation bisphenol A diglycidyl ether, 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexane carboxylate, 3,4-epoxy-1-methylcyclohexyl 3,4-epoxy-1-methylcyclohexane carboxylate, 6-methyl-3,4-epoxycyclohexylmethyl 6-methyl-3,4-epoxy cyclohexane carboxylate, The 3,4-epoxy-3-methylcyclohexylmethyl- 3, 4-epoxy-3-methylcyclohexane carboxylate, 3,4-epoxy-5-methylcyclohexylmethyl-3,4-epoxy-5-methylcyclohexane carboxylate, 2-(3,4-epoxycyclohexyl 5,5-spiro3,4-epoxy) cyclohexane-metadioxane, A bis(3, 4-epoxycyclohexylmethyl)horse mackerel peat, vinylcyclohexene dioxide, 4-vinylepoxy cyclohexane, a bis(3,4-epoxy-6-methylcyclohexylmethyl)horse mackerel peat, 3,4-epoxy-6-methylcyclohexyl carboxylate, methylenebis (3,4-epoxy cyclohexane), Dicyclopentadiene diepoxide, ethylene GURIKORUJI (3,4-epoxycyclohexylmethyl) ether, An ethylene screw (3,4-epoxy cyclohexane carboxylate), epoxy hexahydrophthalic acid dioctyl, epoxy hexahydrophthalic acid di-2-ethylhexyl, etc. are mentioned.

[0046]As an example of said aliphatic series epoxy resin, Aliphatic polyhydric alcohol or poly glycidyl ether of the alkylene oxide adduct, The homopolymer compounded by the vinyl polymerization of poly glycidyl ester of aliphatic series long chain polybasic acid, glycidyl acrylate, or glycidyl methacrylate, The copolymer etc. which were compounded by the vinyl polymerization of glycidyl acrylate or glycidyl methacrylate, and other vinyl monomers are mentioned. As a typical compound, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, triglycidyl ether of glycerin, Triglycidyl ether of trimethylolpropane, tetraglycidyl ether of sorbitol, Hexa glycidyl ether of dipentaerythritol, diglycidyl ether of a polyethylene glycol, Glycidyl ether of polyhydric alcohol, such as diglycidyl ether of a polypropylene glycol, Poly glycidyl ether of the polyether polyol obtained by adding one sort or two sorts or more of alkylene oxide to aliphatic polyhydric alcohol, such as propylene glycol, trimethylolpropane, and glycerin, Diglycidyl ester of aliphatic series long chain dibasic acid is mentioned. Monoglycidyl ether and phenol of aliphatic higher alcohol, Cresol, butylphenol, and monoglycidyl ether of the polyether alcohol obtained by adding alkylene oxide to these, Glycidyl ester of higher fatty acid, epoxidized soybean oil, epoxy stearic acid octyl, epoxy butyl stearate, the epoxidation linseed oil, epoxidation polybutadiene, etc. are mentioned.

[0047]As examples other than the epoxy compound of cationic polymerization nature organic substances other than the compound which has an oxetane ring in (3) molecules which can be used by this invention, Trioxanes, such as a tetrahydrofuran and a 2,3-dimethyltetrahydrofuran, Cyclic ether compounds, such as 1,3-dioxolane and 1,3,6-trioxa

cyclooctane, Annular lactone compounds, such as beta propiolactone, gamma-butyrolactone, and epsilon-caprolactone, Thirane compounds, such as an ethylene sulfide, a trimethylene sulfide, Annular thioether compounds, such as thiethane compounds, such as 3 and 3-dimethyl thiethane, and a tetrahydrothiophene derivative, The spiroortho ester compound obtained by the reaction of an epoxy compound and lactone, A spiro alt.carbo NATO compound, an annular carbo NATO compound, ethylene glycol divinyl ether, Alkyl vinyl ether, 3,4-dihydropyran-2-methyl (3,4-dihydropyran-2-carboxylate), An ethylenic unsaturated compound, the above-mentioned derivatives, etc., such as vinyl ether compounds, such as triethylene glycol divinyl ether, styrene, a vinylcyclohexene, isobutylene, and polybutadiene, are mentioned.

[0048]The epoxy compound which has cyclohexaneoxide structure in < molecule in cationic polymerization nature organic substances other than the compound which has an oxetane ring in the above-mentioned (3) molecules, It is preferred especially to use 50 or more weight sections to the cationic polymerization nature organic substance whole quantity other than the compound which has an oxetane ring into a molecule. The remaining ingredients of 50 or less weight sections may be other epoxy resins and other cationic polymerization nature organic substances.

[0049]In this invention, the loadings of cationic polymerization nature organic substances other than the compound which has an oxetane ring in (3) molecules, (1) It is preferred that they are 500 or less weight sections to cationic polymerization nature organic substance 100 weight section which has an oxetane ring in a molecule, and it is preferred that they are especially 200 or less weight sections. Hardenability is not enough if more than 500 weight sections.

[0050]The loadings of (2) energy-line susceptibility cationic initiator, (1) It is 0.05 - 10 weight section to the total amount of the cationic polymerization nature organic substance which has an oxetane ring in a molecule, and cationic polymerization nature organic substances other than the compound which has an oxetane ring in (3) molecules, and is 0.5 - 10 weight section preferably. If less than 0.1 weight sections, this resin curing thing does not harden enough, and if more than ten weight sections, the resin which has sufficient intensity will not be obtained.

[0051]With (4) radical-polymerization nature organic compound used for this invention. It is a compound which is polymers-izing or a radical polymerization nature organic compound which carries out crosslinking reaction, and has at least one or more unsaturated double bonds in one molecule preferably by energy-line exposure under existence of an energy-line susceptibility radical polymerization initiator.

[0052]As this compound, an acrylate compound, a methacrylate compound, an allyl urethane compound, an unsaturated polyester compound, a styrene system compound, etc. are mentioned, for example.

[0053]Composition and acquisition are easy, and handling is also easy acquisition, and the

compound which has a meta-(acrylic) group also in this radical polymerization nature organic compound has them. [preferred] For example, the acrylic ester (meta) of epoxy (meta) acrylate, urethane (meta) acrylate, polyester (meta) acrylate, polyether (meta) acrylate, and alcohols is mentioned.

[0054] Here, epoxy (meta) acrylate is acrylate produced by making publicly known aromatic epoxy resin, cycloaliphatic epoxy resin, an aliphatic series epoxy resin, etc. and acrylic acid (meta) react for example, conventionally. Especially a desirable thing among these epoxy acrylate, It is acrylate of aromatic epoxy resin and is acrylate produced by making the polyhydric phenol which has at least one nucleus, or poly glycidyl ether of the alkylene oxide adduct react to acrylic acid (meta) (meta). For example, bisphenol A or the glycidyl ether obtained by the reaction of the alkylene oxide adduct and epichlorohydrin, (Meta) The acrylate produced by making react to acrylic acid (meta), the acrylate produced by reacting acrylic acid (meta) to epoxy novolak resin (meta), etc. are mentioned. A thing desirable as urethane (meta) acrylate, The acrylate produced by making hydroxyl group content (meta) acrylic ester and isocyanates react to one sort or two sorts or more of hydroxyl group content polyester and polyethers containing hydroxyl group (meta), It is acrylate etc. which are produced by making isocyanates react to hydroxyl group content (meta) acrylic ester (meta).

[0055] A thing desirable as hydroxyl group content polyester used here, By the reaction of one sort or two sorts or more of polyhydric alcohol, and one sort or two sorts or more of polybasic acid, are hydroxyl group content polyester obtained and as aliphatic polyhydric alcohol, For example, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, A diethylene glycol, triethylene glycol, neopentyl glycol, a polyethylene glycol, a polypropylene glycol, polybutylene glycol, trimethylolpropane, glycerin, pentaerythritol, dipentaerythritol, etc. are mentioned. As polybasic acid, adipic acid, terephthalic acid, phthalic anhydride, trimellitic acid, etc. are mentioned, for example.

[0056] A thing desirable as a polyether containing hydroxyl group is a polyether containing hydroxyl group obtained by adding one sort or two sorts or more of alkylene oxide to polyhydric alcohol, and can illustrate the thing same as polyhydric alcohol as the compound mentioned above. As alkylene oxide, ethyleneoxide, propylene oxide, and butylene oxide are mentioned, for example.

[0057] A thing desirable as hydroxyl group content (meta) acrylic ester is hydroxyl group content (meta) acrylic ester obtained by the esterification reaction of polyhydric alcohol and acrylic acid (meta), and can illustrate the thing same as polyhydric alcohol as the compound mentioned above.

[0058] Especially the hydroxyl group content (meta) acrylic ester obtained by the esterification reaction of dihydric alcohol and acrylic acid (meta) among these hydroxyl group content (meta) acrylic acid is preferred, for example, 2-hydroxyethyl (meta) acrylate is mentioned.

[0059]as isocyanates, the compound which has at least one or more isocyanate groups in a molecule is preferred -- divalent isocyanate compounds, such as tolylene diisocyanate, hexamethylene di-isocyanate, isophorone diisocyanate, -- 101025 -- it is especially desirable. [0060]A thing desirable as polyester (meta) acrylate is polyester (meta) acrylate produced by making hydroxyl group content polyester and acrylic acid (meta) react. A thing desirable as hydroxyl group content polyester used here, It is hydroxyl group content polyester obtained by the esterification reaction of one sort or two sorts or more of polyhydric alcohol, and one sort or two sorts or more of monobasic acids and polybasic acid, and the thing same as polyhydric alcohol as the compound mentioned above can be illustrated. As a monobasic acid, formic acid, acetic acid, butanoic acid, and benzoic acid are mentioned, for example. As polybasic acid, terephthalic acid, phthalic anhydride, and trimellitic acid are mentioned, for example.

[0061]A thing desirable as polyether (meta) acrylate is polyether (meta) acrylate produced by making a polyether containing hydroxyl group and meta-(acrylic) acid react. A thing desirable as a polyether containing hydroxyl group used here is a polyether containing hydroxyl group obtained by adding one sort or two sorts or more of alkylene oxide to polyhydric alcohol, and can illustrate the thing same as polyhydric alcohol as the compound mentioned above. As alkylene oxide, ethyleneoxide, propylene oxide, and butylene oxide are mentioned, for example.

[0062]A thing desirable as acrylic ester (meta) of alcohols, Aromatic series or fatty alcohol which has at least one hydroxyl group in a molecule, And it is acrylate produced by making the alkylene oxide adduct and acrylic acid (meta) react (meta), For example, 2-ethylhexyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, isoamyl (meta) acrylate, Lauryl (meta) acrylate, stearyl (meta) acrylate, Isooctyl (meta) acrylate, tetrahydrofurfuryl (meta) acrylate, IsoBONIRU (meta) acrylate, benzyl (meta) acrylate, 1, 3-butanediol di(metha)acrylate, 1, 4-butanediol di(metha)acrylate, 1,6-hexanediol di(metha) acrylate, diethylene GURIKORUJI (meta) acrylate, Triethylene glycol di(metha)acrylate, neopentyl glycol di(metha)acrylate, poly ethylene glycol di(metha)acrylate, poly propyleneglycol di(meth) acrylate, TORIMECHI roll pro pantry (meta) acrylate, ethyleneoxide denaturation TORIMECHI roll pro pantry (meta) acrylate, Propylene oxide denaturation TORIMECHI roll pro pantry (meta) acrylate, Pentaerythritol tetra (meta) acrylate, dipentaerythritol hexa (meta) acrylate, epsilon-caprolactone denaturation, and dipentaerythritol hexa (meta) acrylate are mentioned.

[0063]It is preferred that 50 or more weight sections in radical polymerization nature organic compound 100 weight section are the compounds which have an acrylic group (meta) in a molecule.

[0064]As for combination of (4) radical-polymerization nature organic compound in this

invention, it is preferred that they are 200 or less weight sections to cationic polymerization nature organic substance 100 weight section, and it is preferred that they are especially 100 or less weight sections.

[0065](4) The resin composition of this invention which blended the radical polymerization nature organic compound becomes a thing which has it and in which the cure rate at the time of performing optical solid modeling rises further compared with the case where these are not blended. [desirable as a resin composition for optical solid modeling]

[0066](5) energy-line susceptibility radical polymerization initiator used for this invention is a compound with possible making a radical polymerization start by an energy ray, and its ketone system compounds, such as an acetophenone series compound, a benzyl system compound, and a thioxan ton system compound, are preferred.

[0067]As an acetophenone series compound, for example A diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 4'-isopropyl-2-hydroxy-2-methylpropiohenone, 2-hydroxymethyl-2-methylpropiohenone, 2,2-dimethoxy-1,2-diphenylethan 1-one, p-dimethylamino acetophenone, p-tertiarybutyl dichloroacetophenone, p-tertiarybutyl trichloroacetophenone, p-azide benzal acetophenone, 1-hydroxycyclohexylphenyl ketone, the 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropanone 1, 2-benzyl-2-dimethylamino 1-(4-morpholinophenyl)- The butanone- 1, benzoin, Benzoin methyl ether, benzoin ethyl ether, benzoin iso-propyl ether, benzoin n-butyl ether, benzoin isobutyl ether, etc. are mentioned.

[0068]Benzyl, anisyl, etc. are mentioned as a benzyl system compound.

[0069]As a benzophenone series compound, benzophenone, methyl o-benzoylbenzoate, a Michler's ketone, 4,4'-screw diethylamino benzophenone, 4,4'-dichlorobenzophenone, 4-benzoyl-4'-methyl-di phenylsulfide, etc. are mentioned, for example.

[0070]As a thioxan ton system compound, thioxan ton, 2-methylthio xanthone, 2-ethyl thioxan ton, 2-chloro thioxan ton, 2-isopropyl thioxan ton, 2, and 4-diethylthio xanthone etc. are mentioned.

[0071]As other (5) energy-line susceptibility radical polymerization initiators, 2,4,6-trimethyl benzoyldiphenyl phosphine oxide, bis(cyclopentadienyl)-bis[2,6-difluoro-3- (****- 1-yl)] titanium, etc. are mentioned.

[0072]These (5) energy-line susceptibility radical polymerization initiators can blend and use one sort or two sorts or more of things according to desired performance.

[0073]Compared with the case where the resin composition of this invention which blended these (5) energy-line susceptibility radical polymerization initiator does not blend these, the cure rate at the time of performing optical solid modeling rises further, and it will become desirable as a resin composition for optical solid modeling.

[0074]The above (5) energy susceptibility radical polymerization initiators are preferably blended 0.1 to 10% of the weight 0.05 to 10% of the weight to (4) radical-polymerization nature

organic compound. If the hardened material which has sufficient intensity when it exceeds this range is not obtained but is less, resin will not harden enough.

[0075]Although it is not indispensable, a photosensitizer etc. can be blended with the resin composition for optical solid modeling of this invention if needed. For example, by using together photosensitizers, such as an anthracene derivative and a pyrene derivative, the cure rate at the time of performing the Mitsuzo form compared with the case where these are not blended improves further, and will become desirable as a resin composition.

[0076]Although it is not indispensable, the organic compound which has two or more hydroxyl groups in one molecule if needed can be blended with the resin composition for optical solid modeling of this invention. For example, the impact strength of shaping material can be raised by blending the organic compound which has two or more hydroxyl groups into one molecule, such as polyhydric alcohol, a polyether containing hydroxyl group, hydroxyl group content polyester, and polyhydric phenol.

[0077]As an example of polyhydric alcohol, ethylene glycol, propylene glycol, Neopentyl glycol, trimethylolpropane, glycerin, pentaerythritol, a dipenta ERISURU toll, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, etc. are mentioned.

[0078]A polyether containing hydroxyl group is a compound produced by adding one sort or two sorts or more of alkylene oxide to one sort or two sorts or more of polyhydric alcohol or polyhydric phenol. As an example of the polyhydric alcohol used for this, Ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, glycerin, pentaerythritol, a dipenta ERISURU toll, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, etc. are mentioned. As an example of polyhydric phenol, bisphenol A, the bisphenol F, phenol novolak resin, cresol novolak resin, etc. are mentioned. Butylene oxide, propylene oxide, ethyleneoxide, etc. are mentioned as an example of alkylene oxide.

[0079]The hydroxyl group content polyester obtained with hydroxyl group content polyester by an esterification reaction with one sort or two sorts or more of polyhydric alcohol and polyhydric phenol, one sort, or two sorts or more of monobasic acids, or polybasic acid, And it is hydroxyl group content polyester obtained by the esterification reaction of one sort or two sorts or more of polyhydric alcohol and polyhydric phenol, one sort, or two sorts or more of lactone. The above-mentioned thing and the same thing are mentioned as an example of polyhydric alcohol or polyhydric phenol. As a monobasic acid, formic acid, acetic acid, butanoic acid, benzoic acid, etc. are mentioned. As polybasic acid, adipic acid, terephthalic acid, trimellitic acid, etc. are mentioned, for example. Beta propiolactone, gamma-butyrolactone, epsilon-caprolactone, etc. are mentioned as lactone.

[0080]Polyhydric phenol is a compound which contains the hydroxyl group coupled directly with the aromatic ring in [two or more] one molecule, and the above-mentioned thing and the same thing are mentioned.

[0081]Although it is not indispensable, a thermoplastic polymer compound can be blended with the resin composition for optical solid modeling of this invention if needed. A thermoplastic polymer compound is a fluid or a solid in a room temperature, and is a high molecular compound mixed with a resin composition in a room temperature at homogeneity.

[0082]As a typical thing of this thermoplastic polymer compound, Polyester, polyvinyl acetate, polyvinyl chloride, polybutadiene, Poly carbo NATO, polystyrene, polyvinyl ether, a polyvinyl butyral, polyacrylate, polymethylmethacrylate, polybutene, a styrene butadiene block copolymer hydrogenation thing, etc. are mentioned. The thing which introduced functional groups, such as a hydroxyl group, a carboxyl group, a vinyl group, and an epoxy group, into these thermoplastic polymer compounds can also be used. Desirable number average molecular weights are [as opposed to / thermoplastic polymer compound / this / this invention] 1000-500000, and still more desirable number average molecular weights are 5000-100000. The effect of improving intensity as it is low molecular weight is not acquired enough, but if it is the amount of polymers, the viscosity of a resin composition becomes high and it becomes impossible to be able to use it, even if it is outside this range, but to call it not much a thing desirable as a resin composition for optical solid modeling.

[0083]Compared with the case where these are not blended, the mechanical physical property of the hardened material at the time of performing optical solid modeling goes up further, and the resin composition of this invention which blended the thermoplastic polymer compound will become desirable as a resin composition for optical solid modeling.

[0084]Although it is not indispensable, a bulking agent can be blended with the resin composition for optical solid modeling of this invention if needed. Bulking agents are inorganic and organic powder, the shape of a flake, and fibrous material.

[0085]As an example of an inorganic bulking agent, glass powder, mica powder, silica, or the end of quartz powder, The end of carbon powder, calcium carbonate powder, alumina powder, aluminum hydroxide powder, Aluminum silicate powder, zirconium silicate powder, iron oxide powder, barium sulfate powder, Kaolin, dolomite, metal powder, glass fiber, carbon fiber, asbestos, a metal whisker, a calcium carbonate whisker, hollow glass balloons, or these surfaces are processed by a coupling agent, and what attached the organic group to the surface is mentioned.

[0086]As an example of an organic bulking agent, pulp powder, nylon powder, polyethylene powder, What attached the reactant basis of an epoxy group, an acrylic group, a hydroxyl group, etc. to bridge construction polystyrene powder, bridge construction acrylic resin powder, bridge construction phenol resin powder, bridge construction urea resin powder, bridge construction melamine resin powder, bridge construction epoxy resin powder, rubber crumbs, or these surfaces is mentioned.

[0087]Unless hardening of this invention is spoiled, various resin additives, such as colorant,

such as a feeling-of-heat reactive cationic initiator, paints, and a color, a leveling agent, a defoaming agent, a thickener, fire retardant, an antioxidant, and stabilizer, etc. can be added. As the above-mentioned feeling-of-heat reactive cationic initiator, JP,57-49613,A and aliphatic series onium salt given in JP,58-37004,A are mentioned, for example.

[0088]the compound which contains two or more hydroxyl groups in the above one molecule by request in this invention in the range which does not check the effect of this invention.

Although various resin additives, such as a thermoplastic polymer compound, a bulking agent, a feeling-of-heat reactive cationic initiator, paints, a color, colorant, a leveling agent, a defoaming agent, a thickener, fire retardant, an antioxidant, and stabilizer, etc. can be used together in the range of anticipated use, In respect of distortion of shaping material, it is preferred to consider it as 200 or less % of the weight to the total amount of the resin composition for Mitsuzo forms of this invention.

[0089]As an activity energy line which stiffens the resin composition of this invention, there are ultraviolet rays, an electron beam, X-rays, radiation, high frequency, etc., and ultraviolet rays are economically the most preferred. As a light source of ultraviolet rays, although there are ultraviolet laser and mercury lamp, a xenon lamp, a sodium lamp, an alkaline metal lamp, etc., since condensing nature is good, especially a laser beam is preferred.

[0090]Next, the optical solid modeling method of this invention is explained in full detail. In order to perform the optical solid modeling method of this invention, as an indispensable constituent first, (1) The cationic polymerization nature organic substance, (2) energy-line susceptibility cationic initiator which have an oxetane ring in a molecule, The resin composition for optical solid modeling methods is obtained from the material of (4) radical-polymerization nature organic substance, (5) energy-line susceptibility radical polymerization initiator, and others cationic polymerization nature organic substances other than the compound which has an oxetane ring in (3) molecules if needed, and also if needed.

[0091]Although this process is good to be based on a well-known process, such materials are mixed enough, for example. The agitating method, the roll kneading crowded method, etc. for using the churning power accompanying rotation of a propeller as a concrete mixing method, for example are mentioned. The above (1) The same range or kind as what described the resin composition for optical solid modeling of this invention can be used for the kind of additive agent blended the desirable compounding ratio of - (5), and if needed, and its compounding ratio. Thus, the obtained resin composition for optical solid modeling is liquefied at ordinary temperature in general.

[0092]Next, irradiate with an energy line, make the arbitrary surfaces of the above-mentioned resin composition harden the energy-line exposure surface of this resin composition, form the hardening layer of desired thickness in them, and the above-mentioned energy-line hardenability resin composition is further supplied on this hardening layer, Lamination

operation of obtaining the hardening layer which stiffened this similarly and followed the above-mentioned hardening layer is performed, and a three-dimensional solid thing is obtained by repeating this operation. Storing the above-mentioned resin composition in a container which is indicated, for example in the JP,60-2475,A I No. 5 gazette, inserting a transparent material in the resin composition surface concerned, and moving said container and the transparent material concerned relatively, if an example is shown. It is the method of forming the solid of desired shape, by supplying an activity energy line required for hardening to the resin composition surface concerned selectively via this transparent material.

[0093]The kind of activity energy line used for the optical solid modeling method of this invention is the same as the activity energy line which stiffens the resin composition of this invention. That is, there are ultraviolet rays, an electron beam, X-rays, radiation, high frequency, etc., and it is economically the most desirable in ultraviolet rays. As a light source of ultraviolet rays, although there are ultraviolet laser, a mercury lamp, a xenon lamp, a sodium lamp, an alkaline metal lamp, etc., since condensing nature is good, especially a laser beam is preferred.

[0094]

[Example]Hereafter, an example and a comparative example explain this invention concretely. By this example, a "part" shall mean a "weight section."

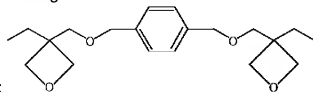
The oxetane 1 shown with a following formula as a cationic polymerization nature organic substance (it omits the following "oxetane") which has an oxetane ring in example 1(1) molecule 85 copies, Three copies are used [the oxetane 2] for 4 and 4' bis-(diphenylsulfonio) phenylsulfide bis-hexafluoroantimonate as 15 copies and a (2) energy-line susceptibility cationic initiator (it omits the following "cationic initiator"), These were mixed enough and the resin composition for optical solid modeling was obtained. The obtained resin composition was a fluid of light yellow transparency.

[0095]Next, the three-dimensional NC (numerical control) table and ultraviolet Ar ion laser (the wavelength 333, the multiline of 351 or 364 nm, output of 100 mW) which carried the container into which the obtained resin composition is put, Using the solid modeling experiment system which consists of a control section consisting mainly of an optical system and the computer for control, it laminated in a 0.1-mm pitch from this resin composition based on CAD data, and a hollow cylinder-like model 10 cm in height and 4 cm in diameter was produced. The time taken to produce this model was 60 minutes. The accuracy to a designed size was 0.022% in the radial direction 0.051% in the height direction.

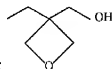
[0096]The resin composition for optical solid modeling of Examples 2-12 was hereafter prepared by the presentation of the resin shown in the following table 1, and it examined by the operation same also about these constituents as Example 1. A test result is written together to Table 1. The constituent was prepared by the presentation of the resin shown in the following

table 2 as a comparative example (comparative examples 1-4), and it examined in the same way as an example. A test result is written together to Table 2. The compound used by each example and a comparative example is as follows.

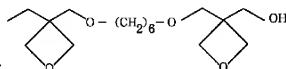
[0097]The following oxetane 1-4 was used as oxetane.



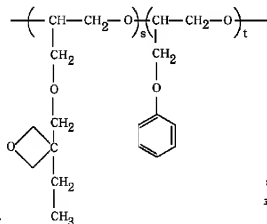
Oxetane 1 :



Oxetane 2 :



Oxetane 3 :



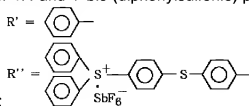
Oxetane 4 :

s : t = 50 : 50

平均分子量 10000

[0098]As a cationic initiator, the following cationic initiators 1-3 were used.

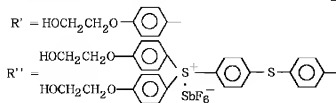
Cationic initiator 1:4 and 4' bis-(diphenylsulfonio) phenylsulfide bis-hexafluoroantimonate



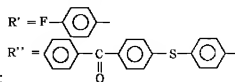
$[R'_2R''S]^+[B]^-$:

B=SbF₆ [0099]The cationic initiator 2:4, 4' bis-phenylsulfide [JI (beta-hydroxyethoxy)

phenylsulfonio]] bis-hexafluoroantimonate $[R'_2R''S]^+[B]^-$:



$B=\text{SbF}_6$ [0100] Cationic initiator 3:4-phenyl-[4'-(benzoyl) phenylthio]] di-(4-fluorophenyl)



sulfoniumhexafluoroantimonate $[R'_2R''S]^+[B]^-$:

$B=\text{SbF}_6$ [0101] (3) As cationic polymerization nature organic substances (it omits the following "cation resin") other than the compound which has an oxetane ring, the following cation resin 1-3 was used into the molecule.

Cation-resin 1: 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexane carboxylate cation-resin 2: 1,4-butane JIORUJ glycidyl-ether cation resin 3: Bis(3, 4-epoxycyclohexylmethyl)horse mackerel peat [0102] (4) As a radical polymerization nature organic substance (it omits the following "radical resin"), the following radical resin 1-3 was used.

Radical Resin 1: Bisphenol-A-diglycidyl-ether-diacylate radical resin 2: trimethylolpropane-triacylate radical resin 3: Dipentaerythritol hexaacylate [0103] (5) The following radical initiators 1 and 2 were used as an energy-line susceptibility radical polymerization initiator (it omits the following "radical initiator").

Radical initiator 1: 1-hydroxy-cyclohexyl-phenyl-KETONRAJIKARU initiator 2: 2,2-dimethoxy-1,2-diphenylmethan 1-one [0104]

[Table 1]

		実施 例1	実施 例2	実施 例3	実施 例4	実施 例5	実施 例6	実施 例7	実施 例8	実施 例9
(1)	オキセタン1	85		25	80	15	30	60		30
	オキセタン2	15	15	50		10	10			
	オキセタン3		85	25					40	
	オキセタン4									
(2)	カチオン開始剤1	3			3		3	1		1
	カチオン開始剤2		2			2			1	
	カチオン開始剤3			3						
(3)	カチオン樹脂1				20			20		
	カチオン樹脂2						10			50
	カチオン樹脂3					75				10
(4)	ラジカル樹脂1						50		50	
	ラジカル樹脂2							10	10	
	ラジカル樹脂3							10		10
(5)	ラジカル開始剤1						5		2	2
	ラジカル開始剤2							3		
作製時間 (分)		60	60	70	63	55	68	55	68	60
精度 (高さ方向、%)		0.051	0.06	0.07	0.056	0.067	0.054	0.048	0.055	0.06
精度		0.022	0.02	0.03	0.025	0.023	0.024	0.031	0.019	0.024

[0105]

[Table 2]

		実施 例 10	実施 例 11	実施 例 12	比較 例 1	比較 例 2	比較 例 3	比較 例 4
(1)	オキセタン 1	10						
	オキセタン 2			20				
	オキセタン 3							
	オキセタン 4		50	50				
(2)	カチオン開始剤 1	2	1	2	1	1		
	カチオン開始剤 2						1	
	カチオン開始剤 3							
(3)	カチオン樹脂 1	40		20	80	60		
	カチオン樹脂 2		50		20	20	20	
	カチオン樹脂 3						30	
(4)	ラジカル樹脂 1	20		10		20		50
	ラジカル樹脂 2	30						
	ラジカル樹脂 3						50	50
(5)	ラジカル開始剤 1			1		1		
	ラジカル開始剤 2	1					1	1
作製時間 (分)		65	50	48	120	115	110	90
精度 (高さ方向、%)		0.05	0.035	0.034	0.08	0.06	0.09	0.10
精度		0.026	0.015	0.018	0.031	0.035	0.04	0.80

[0106]

[Effect of the Invention]As explained above, the hardening inhibition by oxygen does not take place in the resin composition for optical modeling of this invention, but postcure processing is unnecessary, there is little modification, the contraction at the time of hardening is also small, and is easy to obtain the shaping material of a desired size, and, moreover, it has high sensitivity to irradiation energy. Therefore, it can use conveniently for an optical solid molding method.

[Translation done.]